EVIDENCE FROM CRYSTAL STRUCTURES IN REGARD TO ATOMIC STRUCTURES[1]

By Maurice L. Huggins[2]

Abstract

The distribution of valence electrons in the diamond and similar crystals.—Because of the cubical symmetry, the equivalent scattering power of all the atoms, and the absence of pyro- and piezo-electric effect, the atoms in the diamond cannot be held together as a result of the transfer of electrons from atom to atom. Symmetry requirements also eliminate any cubical arrangement of electrons or orbits around each atom. The diamagnetism of H_2 and of most organic compounds eliminates rotations of two electrons or orbits in the same direction about each atomic center-line as a means of holding the atoms together. Similar structures and numbers of valence electrons, together with interatomic distance comparisons, indicate that the atoms in BeO, ZnO, ZnS, CdS, AgI, etc., are held together in a manner similar to that in the diamond. If so, there cannot be four electrons rotating around each atomic kernel in the diamond, for Zn^{--}, Ag^{---}, O^{++} etc., are chemically impossible. It is not possible for two electrons to be rotating about each two adjacent atomic kernels in crystals of NaCl, MgO, CdO, AgBr, etc., and since chemically and physically these are not very different from BeO, CdS, AgI, etc., the bonds in the last named crystals and so in the diamond are probably not of this type. The conclusion is therefore reached that in the diamond and crystals of similar structure, the electrons are in pairs at tetrahedron corners around each atom, each pair being held jointly by two atoms. This is as predicted from the Lewis theory of valence. A study of the other known crystal structures leads to the conclusion that in general the valence shells of electro-negative atoms are tetrahedra of electron pairs rather than cubes of single electrons.

THIS paper is an attempt to show that important conclusions concerning the ways in which the valence electrons are arranged may be reached from a careful analysis of the structures of some of the simplest crystals.

The diamond. The arrangement[3] of atoms in this substance is pictured in Figs. 1 and 5. Each carbon atom is surrounded by four others placed around it as are the four corners of a regular tetrahedron around its center. All the atoms are equivalent, both as regards their positions

[1] Some of the material given in this paper has been presented at meetings of the American Physical Society and the American Chemical Society. For abstracts, see Phys. Rev., **21**, 379 (1923) and Science, **57**, 534 (1923). The electron distributions arrived at were proposed by the author in the J. Am. Chem. Soc. **44**, 1841 (1922).

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[3] See Wyckoff, "The Structure of Crystals," Chem. Cat. Co., New York, 1924, for references to the crystal structure work.

in the structure and their ability to scatter x-rays. The symmetry of the structure, as shown by both the crystallographic and the x-ray data, is that of the cubic or isometric system.

There are four valence electrons per atom; our problem is to determine, if possible, how they are distributed.[4] The tetrahedral arrangement around each atom, the stability of the diamond toward disruption by heat or chemical action, its low electrical conductivity, etc., suggest that the atoms in this crystal are held together in the same manner as the carbon atoms in "saturated" organic compounds.[5] The theories which have been proposed for the nature of such a union may be divided

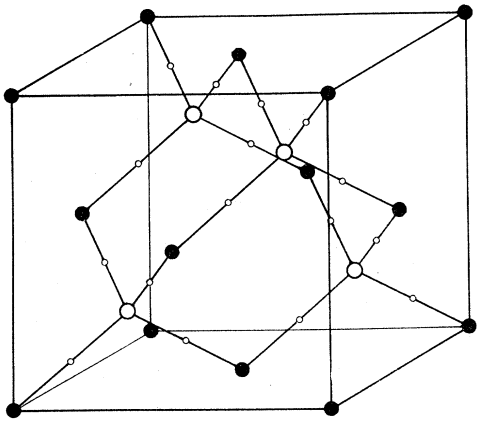

Fig. 1. Unit cube of the diamond, cubic ZnS, etc. In the diamond all atoms are of carbon and the electron pairs, represented by the small circles, are at the mid-points of the atomic centerlines, as shown. In ZnS the Zn atoms are in the positions represented by the large dots, the S atoms are in those represented by the large circles, and the electronpairs are on the centerlines between atoms, but closer to the sulfur than to the zinc.

into two classes, (1) those assuming the transfer of electrons from atom to atom,[6] the individual carbon atoms being represented as $^{+}_{+}C^{+}_{+}$, $^{+}_{+}C^{+}_{-}$,

[4] It would also be of interest to learn how the two K electrons of each atom are placed, but the evidence at hand is insufficient to enable us to do this. The symmetry and x-ray requirements are met if they are so close to the nuclei as not to affect appreciably the symmetry of the arrangement of valence (L) electrons, and either are oriented relative to their nuclei in a random way throughout the crystal or are regularly distributed in a large unit having cubic symmetry.

[5] Such interatomic distance data as are at present available for crystals of organic compounds are also in agreement with this idea. If correct, then the conclusions to be drawn regarding the type of atom-bonding in the diamond are also applicable to the bonds within organic molecules.

[6] Thomson, "The Corpuscular Theory of Matter," Scribner, New York, 1907; Falk and Nelson, J. Am. Chem. Soc. **32,** 1637 (1910); Fry, Zeits. f. Phys. Chem. **76,** 385 (1911); J. Am. Chem. Soc. **34,** 664 (1912); Stieglitz, ibid, **44,** 1293 (1922).

$\overset{+}{-}C\overset{+}{-}$, $\overset{+}{-}C\overset{-}{-}$, or $\overset{-}{-}C\overset{-}{-}$; and (2) those postulating the sharing of electrons between atoms.[7]

Considering now the first of these classes, if the atoms in the diamond were half $\overset{+}{+}C\overset{+}{+}$ and half $\overset{-}{-}C\overset{-}{-}$ they would not have equivalent scattering powers, for those of the first kind would have but two electrons each, while those of the latter would have ten. Furthermore, the [111] faces of the crystal would be electrically polar, the layers of atoms parallel to these faces being alternately positive and negative and spaced as indicated in Fig. 2. This would be made manifest by the presence of

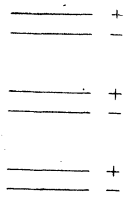

Fig. 2. Spacing of [111] planes in ZnS (also in the diamond, if the atoms were charged).

pyro-electric and piezo-electric effects, as in ZnS, for instance. The same objections apply to a structure consisting of $\overset{+}{+}C\overset{+}{-}$ and $\overset{+}{-}C\overset{-}{-}$ atoms, arranged so that each carbon-carbon bond is positive at one end and negative at the other; there is also the additional objection that the distribution of charges would have the symmetry of the trigonal system rather than that of the cubic or regular system. This would result not only in displacement of the atomic centers in the direction of the three-fold symmetry axis, but in irregular growth, unsymmetrical etch figures, interference figures (produced by polarized light) indicative of the lower symmetry, etc. If all the atoms in the crystal were $\overset{+}{-}C\overset{+}{-}$, held together by electrostatic forces concentrated at the "ends of the bonds," the crystal would have tetragonal symmetry and the [001] faces would be polar, as the positive ends of all the atoms would be turned in the same direction. We thus arrive at our first conclusion, that *the atoms in the diamond are not held together as a result of the transfer of electrons from one atom to another.* This must be true whether the electrons are in or vibrating about fixed positions in the atoms, or are revolving in orbits.

[7] Lewis, J. Am. Chem. Soc. **38,** 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923; Bohr, Phil. Mag. **26,** 857 (1913).

According to the electron-sharing theory, which chemists[8] have found exceedingly useful in accounting for the properties of substances containing non-polar bonds, the kernel of an electronegative atom tends to be surrounded by a valence shell containing eight electrons, and in order to accomplish this result it bonds with other atoms, two electrons (or electron orbits) shared between two atoms constituting a typical "single bond." The eight electrons of a complete shell were at first represented as at corners of a cube, but, in order to account for the triple bond of organic chemistry and for other reasons, the "cubical atom" was later abandoned in favor of the "tetrahedral atom," in which the valence electrons are assumed to be drawn together in pairs.[9]

If each atom in the diamond had a valence shell consisting of a cube of single electrons or electronic orbits (Fig. 3), the crystal would have

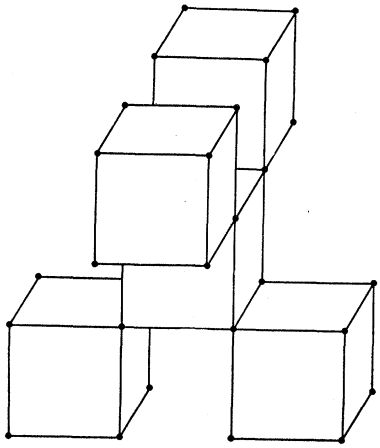

Fig. 3. Cubes edge to edge in a pseudo-diamond type of structure having tetragonal symmetry. The small dots represent single valence electrons.

tetragonal symmetry, for the arrangement in the direction of one of the crystal axes would be different from that in the direction of each of the other two axes. The ratio of the unit distances would be $1:1:\sqrt{2}$, rather than 1:1:1, as is actually the case. *No cubical arrangement of electrons or electron orbits around each atom, with two electrons or orbits shared between each two adjacent atoms, could give a structure for the diamond having the symmetry of the cubic system.*

The minimum elements of symmetry which a crystal must possess in order to belong to the cubic system[10] are four three-fold symmetry

[8] Lewis, Ref. 7; Langmuir, J. Am. Chem. Soc. **41**, 868, 1543 (1919); **42**, 274 (1920); Latimer and Rodebush, ibid. **42**, 1419 (1920); Huggins, ibid. **44**, 1607 (1922).

[9] Lewis, Ref. 7; Huggins, J. Phys. Chem. **26**, 601 (1922).

[10] See any good book on crystallography.

axes and three two-fold symmetry axes. As the observations used to determine the symmetry of crystals—the symmetry of the diffraction effects with light and with x-rays, the rates of growth and solution in different directions, etc.—depend largely (in case of the diamond at least) on the distribution of the valence electrons, we may say with certainty that their distribution must either possess the elements of symmetry just mentioned or there must be a randomness in the arrangement which statistically will produce the observed effects. Inspection of the arrangement of atomic centers in the diamond shows that a distribution of *pairs* of electrons tetrahedrally about each atomic kernel satisfies the symmetry requirements just mentioned, *provided both electrons of each pair are on, or distributed in a random manner about, the straight line connecting the two nearest atomic centers.* The corresponding requirements which must be satisfied by a distribution of electron *orbits* in the diamond may be stated as follows: *Fixed (non-precessing) orbits, other than circular orbits in planes normal to the three-fold axes, are impossible, unless oriented in a random manner about these axes. If there are electron rotations or orbital precessions, they cannot be synchronized with each other throughout the crystal.* If the synchronization were such as to produce one true three-fold symmetry axis there could be no other similar axes in the crystal. In other words, it is impossible to build up any crystal having the cubic symmetry which the diamond is known to possess with *fixed* orbits or *synchronized* precessions or rotations.

Considering now the types of orbital motions not ruled out by the arguments in the foregoing paragraphs, we might imagine adjacent carbon atoms to be held together as a result of rotations of electrons or of orbits about the atomic center-line in one of the ways represented in Fig. 4.[11] If the first were correct, though, and the same type of bonding exists in organic molecules, a large majority of the latter should be paramagnetic. A compound like methane, $H:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:H$, we might expect to be diamagnetic, but it would seem very unlikely that in ethane, $H:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:H$, or in propane, $H:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:H$, for instance, the magnetic effect of each pair could be counterbalanced by the effects of the others. The same argument would of course also apply to molecular hydrogen, if the atoms were held together in the manner of Fig. 4A.[12]

[11] Cf. Lewis, "Valence, Etc." (Ref. 7) p. 59.

[12] Cf. Bohr, Ref. 7.

Moreover, if the bonds in the diamond were of this type, there would be two kinds of atoms. In one all rotations would be clockwise, in the other counter-clockwise, as seen from the center of the atom. (If each atom contained both clockwise and counter-clockwise rotations, the crystal would have trigonal or tetragonal symmetry, as was shown would be the case if the atoms contained both plus and minus charges $-{}^{+}_{-}C^{+}_{-}$ or ${}^{+}_{-}C^{-}_{-}$ and ${}^{+}_{+}C^{+}_{-}$.) Atoms of the first kind could only combine with those of the second kind, and vice versa. If they were held together as indicated in Fig. 4B, all the atoms in a single crystal would be of the same kind, having all the rotations (of the nearest valence electrons) clockwise, for instance, as viewed from the atomic center. There is of course no *a priori* reason for assuming that counter-clockwise atoms could not exist, but they would have to be in a different crystal, for only atoms of like rotational character could combine together. Either

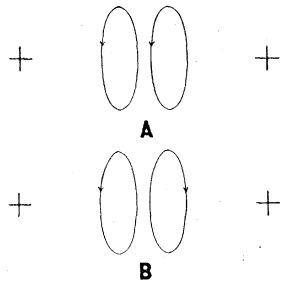

Fig. 4. Representing two types of rotations of valence electrons or orbits about atomic centerlines.

of these two hypotheses would lead to rather fantastic conclusions with regard to organic reactions, but further discussion of this subject is beyond the scope of this paper.

It might be noted in addition that from ordinary electromagnetic theory we should expect repulsion between two electrons of a pair rotating as in Fig. 4B. This would also be true, except in the case of ring electrons, if the electrons were rotating as in Fig. 4A.

In order to proceed further with the elimination of proposed types of interatomic bonds, we shall now consider other closely related structures.

Crystals having structures similar to that of the diamond. Silicon,[13] germanium,[3] and gray tin[3] have been found to have crystal structures of the same type as the diamond. Each of these elements is tetravalent and it seems reasonable to assume four valence electrons per atom and

[13] Ref. 3. Küstner and Remy, Phys. Zeits. **24,** 25 (1923).

that the atoms are held together in the same way as are the carbon atoms in the diamond. Insofar as the chemical and physical properties of these substances are known, they are in accord with these conclusions. The binary compounds ZnS[3], ZnSe[14], ZnTe[15], HgS[16], HgSe[15] HgTe,[15] CdTe[15], CuCl[3], CuBr[3], CuI[3], AgI[3], and AlSb[17], also have the same type of structure, half of the atoms of course being of one kind and half of the other. In ZnS, for example, each zinc atom is surrounded by four sulfur atoms at corners of a regular tetrahedron and each sulfur similarly by four zinc atoms (Figs. 1 and 5).

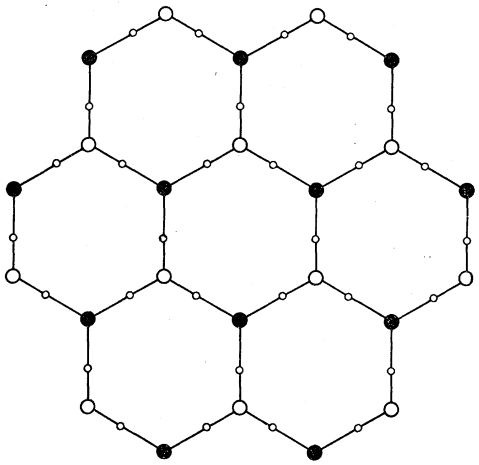

Fig. 5. Representing the distribution of atoms and electronpairs within each layer in crystals of the diamond, ZnS, and ZnO types. The large dots and large circles denote atoms in different planes. In the diamond, Si, etc., all atoms are of the same kind and the electronpairs (small circles) are midway between atomic centers: in ZnO, ZnS, etc., the dots represent atoms of one kind and the large circles those of another, the electronpairs being closer to one kind of atom than to the other, as shown. In crystals of either type each atom is also bonded to another, directly over or under it, in another layer.

A number of other binary compounds, namely AlN[18], BeO[3], ZnO[3], ZnS[3], ZnSe[15], CdS[19], CdSe[15], and AgI[3], possess structures which, although they have the symmetry of the hexagonal system, resemble the cubic structures just mentioned in that each atom is surrounded

[14] Huggins, Phys. Rev. **21,** 211 (1923). Davey, ibid. **21,** 380 (1923).

[15] Huggins, Ref. 14.

[16] Huggins, Ref. 14. Kolkmeijer, Bijvoet and Karssen, Proc. Acad. Sci., Amsterdam, **27,** 390 (1924); Verslag Akad. Wetenschappen **33,** 327 (1924).

[17] Owen and Preston, Proc. Phys. Soc., **36,** 341 (1924).

[18] Ott, Zeits. f. Phys. **22,** 201 (1924).

[19] Ref. 3. Huggins, Ref. 14.

tetrahedrally by four others of opposite character (Cf. Fig. 5). This is probably also true of carborundum (SiC)[20].

In the cubic structures listed above, the tetrahedron of atoms closest to any given atom *must* be regular; in the hexagonal crystals it is also very nearly regular (at least within a percent or two, approximately the limit of error of the experimental determinations). Moreover, in those cases (e.g. ZnS and AgI) in which the same chemical compound crystallizes in both ways, the distance between adjacent atoms (Table I) is almost identically the same in the two crystals.

TABLE I

Interatomic distances in various crystals

Crystal	Distance	Reference
C	1.54A	Bragg[3], Hull[3]
Si	2.34–2.36	Debye and Sherrer[3] Hull[3], Gerlach[3], Küstner and Remy[13]
Ge	2.43; 2.44	Kolkmeijer[3], Hull[3]
Sn	2.80	Bijl and Kolkmeijer[3]
SiC	1.90	Ott[20]
AlN	1.89	Ott[18]
AlSb	2.65	Owen and Preston[17]
BeO	1.65	McKeehan[3]
ZnS, cubic	2.34; 2.35	Gerlach[3], Bragg[3]
ZnS, hexagonal	2.33; 2.36	Aminoff[3]; from density=3.98 (Mourlot[21])
ZnSe	2.45; 2.43	Davey[3]; from density=5.40 (Margottet[22])
ZnTe	2.53	From density =6.34 (Margottet[22])
CuCl	2.32; 2.38	Davey[3]; Wyckoff and Posnjak[3]
CuBr	2.49; 2.52	Davey[3]; Wyckoff and Posnjak[3]
CuI	2.61; 2.63; 2.64	Aminoff[3]; Davey[3]; Wyckoff and Posnjak[3]
AgI, cubic	2.81; 2.83	Wilsey[3]; Davey[3]
AgI, hexagonal	2.81	Aminoff[3]; Wilsey[3]

This, together with the further fact that the physical and chemical properties of the two forms are all almost exactly the same, shows that the atoms in both must be held together in the same way.

If we follow Thomson,[6] Lewis,[7] Kossel,[23] Bury,[24] Bohr,[25] Huggins,[9] Stoner,[26] and others in assigning one valence electron to each atom of an element in Group I of the periodic table, two electrons to each atom of an element in Group II, etc., we find that in all of these crystals there is an average of four electrons per atom, the same as in the diamond, Si, Ge, and Sn. Moreover, as shown by Table I, pairs of crystals

[20] Ott, Naturwissenschaften **13,** 76 (1925). See also Ref. 3.
[21] Mourlot, Ann. d. chim. Phys. **17,** 534 (1899).
[22] Margottet, Compt. rend. **84,** 1293 (1877).
[23] Kossel, Ann. der Physik, **49,** 229 (1916).
[24] Bury, J. Am. Chem. Soc. **43,** 1602 (1921).
[25] Bohr, Zeits. f. Physik **9,** 1 (1922).
[26] Stoner, Phil. Mag. **48,** 719 (1924).

with similar physical and chemical properties (diamond and BeO, Ge and ZnSe, Sn and AgI, and SiC and AlN) have nearly the same interatomic distances.

It seems highly probable then that *the atoms in all of these compounds are held together in a way which is not radically different from that in the diamond.* Any theory of the nature of the bonds between the atoms must be applicable to all of these compounds without necessitating any abrupt change from one type of bond to another. *It would therefore seem very unlikely that in zinc sulfide, for instance, all the valence electrons are in rotation in orbits enclosing the sulfur kernel with none enclosing the zinc kernel,* for such a distribution (of *all* the electrons about *half* the atoms) was shown to be impossible in the diamond, and an abrupt change would be necessitated in going from such a structure to one in which four electrons were rotating around each kernel. By similar reasoning *we must consider extremely improbable any arrangement of four electrons rotating about each atomic kernel* in the diamond, for such a structure for ZnS, BeO, or AgI would require such chemically absurd ions as Zn^{--}, Ag^{---}, O^{++} etc. Moreover, no structure placing but two electrons about each electropositive atom and six about each electronegative atom (in ZnS or BeO) is possible, because a corresponding electron distribution in the diamond could not be correct.

Crystals having the sodium chloride type of structure. The following compounds have been found to have the type of atomic arangement pictured in Fig. 6: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, RbBr, RbI, CsF, MgO, MgS, CaO, CaS, CaSe, SrO, SrS, SrSe, BaO, BaS, BaSe, MnO,[27] MnS, CdO, NiO, CoO, PbS, AgCl, and AgBr.

If we again assume current theories[28] in regard to the number of valence electrons to be correct, we find in each case,[29] as before, an average of four per atom. In these crystals, however, there are *six* equivalent electronegative atoms around each electropositive atom and vice versa, and it is not structurally possible for the atoms to to be held together by electrons rotating in orbits enclosing two nuclei. If the bonds between atoms were of this type in the crystals having structures like the diamond, ZnS and ZnO, we should then expect very decided differences in properties between the two classes of substances. When we compare the properties[30] of BeO and MgO, of CdO and CdS, or of

[27] Levi, Gazz. chim. ital., **54**, 704 (1924).
[28] Ref. 6, 7, 23, 24, 25, 26.
[29] Except, perhaps, in PbS.
[30] See any standard work on inorganic chemistry.

AgBr and AgI, we find no such marked differences. *This observation eliminates from further consideration any structure*, for any of the crystals so far discussed, *in which the atoms are held together by valence electrons in rotation about two atomic centers.*

We have then no alternative but to conclude that, provided the arguments used in the foregoing analysis are valid, *the valence electrons in the diamond and crystals of similar structure*, including those of the zinc oxide type, *are in pairs at tetrahedron corners around each atomic kernel, each electron pair being held jointly by two atoms.* Whether the electrons are in, or oscillating about, equilibrium positions on the atomic centerlines, or are ring electrons or electrons rotating in orbits about these

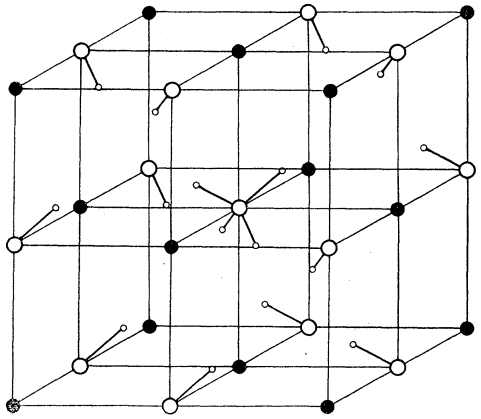

Fig. 6. Unit cube of the sodium chloride structure, showing the probable distribution of the valence electronpairs. The large dots represent sodium kernels and the large circles chlorine kernels. Atoms of either kind, considered separately, are at the points of a face-centered cubic lattice.

centerlines (in the relative directions indicated in Fig. 4B) need not be further discussed at this time.

It has not been shown whether the valence electrons in crystals of the sodium chloride type are in pairs at tetrahedron corners, or singly at cube corners, around the kernels of the electronegative atoms. Certainly, if we had only crystals of this type to consider, the cubical arrangement would seem more likely than the tetrahedral, but the fact that in all the other crystals discussed in this paper and in many more to be dealt with in another article[31] the kernel of each electronegative atom must be surrounded by a tetrahedron of electronpairs makes it seem very probable that this is also the case in these crystals (Fig. 6).

[31] Soon to be published.

As the valence electrons are surely much more tightly held by the kernels of the electronegative atoms (within the valence tetrahedra) than by those of the electropositive atoms, it is often convenient, and an approximation to the truth, to speak of the structure as composed of electropositive and electronegative "ions." Similarly we may speak of the "ions" of beryllium and oxygen in a crystal of BeO, but in either case it should be understood that the valence electrons have not passed *completely* from one atom to another but are mutually held by two or more atoms, also that all degrees of "ionization" (or better, "polarity") are possible, these substances and the diamond being extreme cases.

Other crystals. A study[31] of other crystals of known structure has resulted in the following conclusions:

(1) *In all those which contain electronegative atoms*, excepting only $CsICl_2$, graphite, and certain carbonates and nitrates, *the arrangement is such as to permit a valence shell of 8 electrons around the kernel of each electronegative atom.*

(2) In those which contain electronegative atoms adjacent to each other, excepting only $C(CH_2OH)_4$ and the crystals just mentioned as exceptions to the preceding generalization, valence shells consisting of tetrahedra of electronpairs are possible in full accord with all available data, while cubic valence shells are in FeS_2, MnS_2, Se and Te improbable and in all other cases impossible.

(3) In those containing both electropositive and electronegative atoms, with the latter not adjacent to each other, a comparison of the structures obtained on the assumption of tetrahedral valence shells with those obtained on the assumption of cubical valence shells favors the former as the more probable in nearly every case.

(4) In crystals of the metals, the prevailing tendency seems to be for each atom to surround itself by as many others as possible, the number of valence electrons and the orienting tendencies of the atomic kernels being of minor importance.

In view of the above, it would seem reasonable to assume a tetrahedron of electronpairs as the valence shell of each electronegative atom, whenever such an assumption is not in conflict with x-ray or other evidence. The probable electronic distributions so obtained will be dealt with in detail in another paper.[31]

The Cause of Pairing. Although the author believes that the evidence given in this paper conclusively proves the existence of electronpairs in atomic shells, he is not able to give any satisfactory reason for their existence. There seem to be two alternatives; either there must be an attractive force between electrons at small distances, or the repulsion

between electrons must rapidly decrease with decrease in distance, for distances less than a certain value. The latter alternative would not require electronpairing except in atomic shells, but would qualitatively at least account for the formation of pairs and for the grouping of electrons into distinct shells.

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